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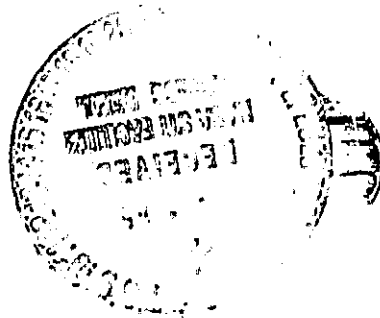
POSITIVE ELECTRODES OF NICKEL-CADMIUM BATTERIES

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16. Abstract Ni hydroxide sintered electrodes which are filled electrochemically are superior to chemically treated electrodes. In the electrochemical process, the hydroxide grows on the Ni grains and possesses a well-defined porous structure. Diffusion and conducting mechanisms are therefore facilitated.

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POSITIVE ELECTRODES OF NICKEL-CADMIUM BATTERIES

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1. Introduction   /68*

Since the nickel-cadmium storage battery was introduced by
Edison [11, 12] and Jungner [24] around the turn of the century,
considerable advances have been obtained in the area of electrode
production. The technology of the tube and pocket plates which
dates back to the technology of Edison was developed to such an
extent that considerable improvements may no longer be expected
[23, 26]. The active mass of the positive electrode (nickel
hydroxide) is mixed with graphite or nickel flakes to achieve
better conductivity and introduced mechanically in bags or tubes
of perforated steel or nickel plate. The current voltage
behavior of cells which are built from such electrodes is no longer
totally satisfactory, primarily under strong load (Figure 1). The
discharge curves of the folded strip electrode developed from the
pocket electrode are also to be considered as "soft".

Sintered electrodes or sinter foil electrodes were developed
for high to extremely high loads. Here carbonyl nickel powder is
sintered bilaterally in a reducing atmosphere on nickel netting
or perforated nickel sheets. Stable plates of definite thickness
are produced with porosities according to grain size and the
production process of up to 80%. These plates, as will be described
briefly hereafter, are filled with active mass by chemical or
electrochemical means. The advantage of such sintered electrodes
as compared with the conventional electrodes resides in the
following:

The distance of two highly conductive layers, for example,

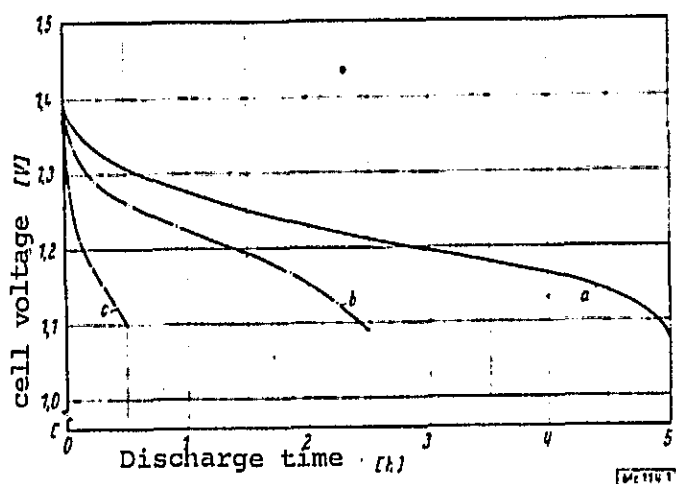*Numbers in the margin indicate pagination in the foreign text.

Figure 1. Discharge curves of a nickel-cadmium cell with pocket electrodes; capacity 3 Ah.
a) for five hours; b) two and a half hours; c) half hour.

in the tubes is about 0.3 mm, the pore diameter of the sintering frame about 5 to 20 μm. The current furnished by the active particles of the tube plate must in the most unfavorable way travel over a path of 0.15 mm to the current arrester, or the sintered plates at most 0.01 mm. The electrical resistance in the sintered plates is therefore much lower. The use of the mass is thus much better; it is about 80% as compared with only 60% for pocket plates. This implies naturally a higher efficiency of sintered cells.

Nickel-cadmium cells with sintered electrodes give discharge curves which may be considered as "hard" characteristics, that is, a moderate voltage remains preserved up to the end of the discharge process. The characteristic curve occurs approximately horizontally. The fact that between the cells which are filled chemically and those activated electrochemically there are still considerable differences in power is shown by Figures 2 and 3. It is striking to note that the plates filled electrochemically according to a method of L. Kandler [25] give an almost ideal characteristic (Figure 3), while those taken from a commercial nickel-cadmium storage battery of comparative chemically filled electrodes have a relatively "soft" discharge curve as regards porosity, thickness and capacity.   /69

The intention of this study is to contribute to the explanation of the particularly good behavior of the electrodes produced by electrochemical methods. To this end we will first describe briefly the competing processes.
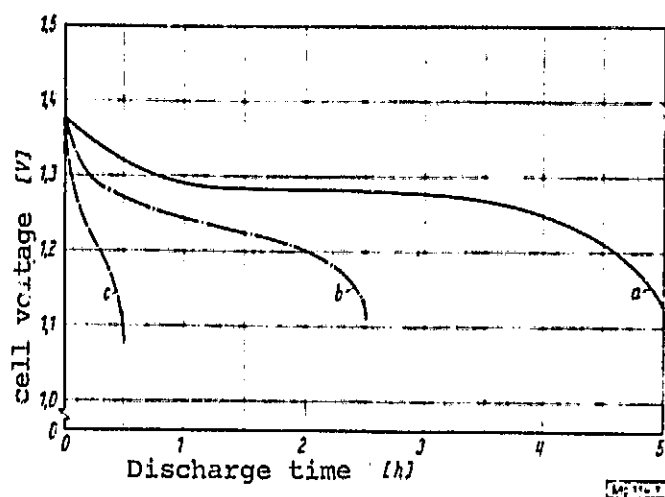
Figure 2. Discharge curves of
a nickel-cadmium cell with
sintered electrodes, active
mass introduced according to
the impregnation method;
capacity 3 Ah.
a) five hours; b) two and a
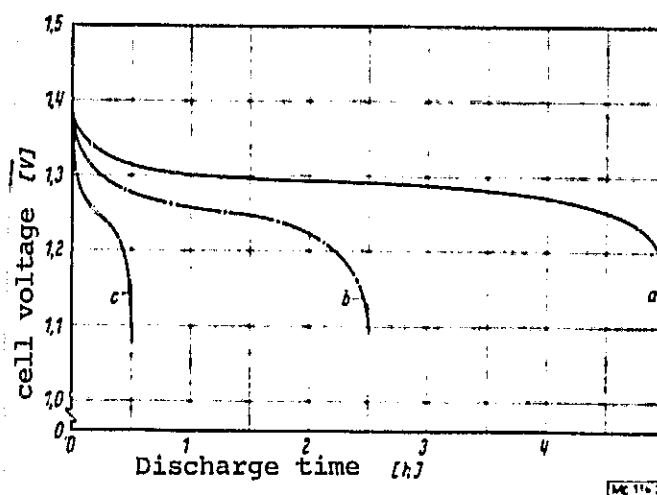half hours; c) half an hour.

Figure 3. Discharge curves of
a nickel-cadmium cell with
sintered electrodes, active
mass introduced electrochemically
according to the Kandler process;
capacity 3 Ah.
a) five hours; b) two and a half
hours; c) half an hour.

2. Method for the Production of Nickel-hydroxide Electrodes

The production of conventional electrodes has in general
been described in detail in most textbooks and some monographs (for
example [13, 16, 26, 47]). The corrosive activation of sintered
material through anodic oxidation in $NaHCO_3$ solutions according
the method of F.A. Schneider [42] will only be mentioned here.

2.1. The Chemical Filling Process

Generally the sintered material is impregnated with acidulated
nickel nitrate solution, circumstances permitting, under vacuum
[16, 17, 38, 18]. The solution contains 240 to 250 g/ℓ nickel,
1--4 g/ℓ HNO_3 and possibly 5--10% cobalt nitrate. If the process
is implemented at 50 to 85°C, vacuum may be omitted.

Now the plates are dried in the air at 85°C. The hydroxide
is precipatated in soda lye of 220--400 g/ℓ at 85°C. After thorough
washing in water at 85°C, air drying is carried out at 100°C.

The method is repeated until the desired amount of active mass has been deposited in the pores of the structure. A complete cycle lasts at least 8 hours, so that the total duration for 5--6 necessary cycles amounts to 40--48 hours and more.

One variant of this process [17] consists in placing the plate after impregnation with nickel nitrate into 20--25% KOH and loading it at a temperature of 70--100°C cathodically with 2--10 A/dm^2. The nitration which is difficult to wash out from the nickel hydroxide precipitate is destroyed cathodically according to the following global equation
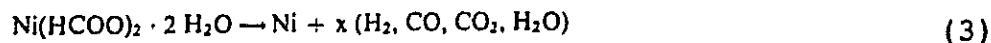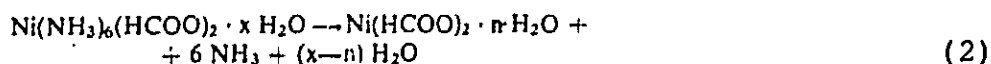
$$NO_3^- + 6 H_2O + 8e^- \rightarrow NH_3 + 9 OH^- \tag{1}$$
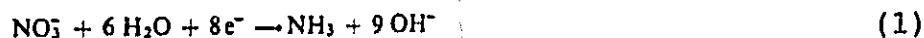
A drying process is thus saved.

2.2. Thermal Decomposition of Nickel Complexes

According to a process recently proposed by K.D. Beccu [3], the sintered material is impregnated with a concentrated solution of nickel hexaminoformate, dried at 90°C and decomposed at 130--220°C in an atmosphere containing water vapor and CO_2. The process is indicated as follows by Beccu:

$$Ni(NH_3)_6(HCOO)_2 \cdot x H_2O \rightarrow Ni(HCOO)_2 \cdot n H_2O + \\ + 6 NH_3 + (x-n) H_2O \tag{2}$$

$$Ni(HCOO)_2 \cdot 2 H_2O \rightarrow Ni + x (H_2, CO, CO_2, H_2O) \tag{3}$$

The active nickel arising (partly also NiO) is converted into nickel hydroxide in several forming cycles in 7 n KOH at about 20 mA/cm^2.

The advantages of the method include the much better solubility of nickel aminoformate as compared with nickel hydroxide and the lower viscosity of the solution. This accelerates an impregnation process and even narrow pore sintered plates up to 3 μm can be

filled without difficulties. In this process 8 to 9 impregnation-destruction cycles, that is about 8 hours are needed, to obtain the starting material for usable positive plates.

2.3. Electrochemical Process

All previously described methods are very time consuming and are not very suitable for production on a continuous basis. In recent years therefore a large number of electrochemical methods were developed, of which some meanwhile have assumed technical importance. Except for one process [4] the electrochemical methods of impregnation of sintered material are based on a basic idea by L. Kandler [25].

2.3.1. The Kandler Process

The principle of this process may be described as follows: by electrolysis in the electrically conductive pore system and in the very close vicinity, a component of the electrolyte is altered in such a way that there is a pH-shift and the corresponding metal hydroxide is precipitated in the pores. By variation of the composition of the bath, the current density, temperature and time of electrolysis may be achieved as the precipitation begins in the depths of the pore system and progresses gradually outwards. The process can therefore be used for a large number of metals, which form insoluble compounds in a not too narrow pH range.

For the electrochemical impregnation of nickel structures with nickel hydroxide according to the Kandler method, the following processes have proved satisfactory [22, 25]: the porous plate is placed between pure nickel anodes as a cathode in a electrolyte, which contains 100 g/ℓ Ni(NO$_3$)$_2$ · 6H$_2$0. By adding HNO$_3$ a pH value of 2--3 is adjusted and maintained. In most cases several percent of nitrate is still contained and according to the special re-quirements for the electrode, other metal additives also. The eletrolysis is carried out at 25°C with a current density of 0.5 A/dm^2. The electrolysis lasts about 8 hours for 1 .mm thick

electrodes with porosity of about 80%. This is followed by a 1 hour cathodic treatment of sintered electrodes at 20% KOH with a current density of about 5 A/dm^2. Here the excess nitrate ion in the pores and hydroxide particles is destroyed quantitatively and converted into NH$_3$ (see equation (1)).

Figure 3 shows the discharge behavior of a nickel-cadmium cell produced by this process. The sintered material has porosity of about 80% in a plate thickness of 1.1 mm. The capacity for a 1 hour discharge corresponds to 1.65±0.05 Ah/dm^2 per cell, that is 3 Ah.

Some authors have tried to clarify the electrochemical processes in the Kandler process [22, 25, 32, 35 and 35]. The most illuminating so far seems to be the explanation of L. Kandler and E. Häusler [25, 22]. According to them two processes take place side by side at the cathode:

evolution of hydrogen

$$2\,H^+ + 2e^- \longrightarrow H_2 \tag{4}$$

and reduction of nitrate

$$NO_3^- + 10\,H^+ + 8e^- \longrightarrow NH_4^+ + 3\,H_2O \tag{5}$$
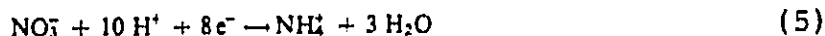
Since the redox potential of (5) is much more positive than that of the evolution of hydrogen, the nitrate reduction must be preferred. Evolution of hydrogen is observed to a much lower extent only for high current density.

Through the consumption of the hydrogen ion therefore the pH will increase in the pores (while in the electrolyte it will remain constant). The deposition of nickel hydroxide now begins at the places at which the prevention of diffusion is greatest, that is in the depths of the pores. The separation of hydroxide on the outside of the electrode is prevented by constant low pH value of the solution. Therefore the pores are filled uniformly

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from inside towards the outside.

As was shown by experiments in our laboratory, with this process it is possible to impregnate even plates up to 5 mm thick homogeneously with a positive mass.

2.3.2. Improvement of the Kandler Process

K. Dehmelt, H. von Döhren and H.H. Kröger [9] describe a modification of the nitrate electrolytes. They use nitrate solutions in which the nickel ion occurs bound in a complex by means of ammonia, aliphatic or aromatic amines. The pH value is 9--12; this high pH value should exclude the possibly occuring corrosion of the nickel structure. The current density is 5 A/dm^2, while electrolysis times of 4 to 5 hours are indicated.

G.A. Mueller [36] shortens the time of the electrolysis to a considerable extent, by using "melted" nickel nitrate hydrate as impregnating solution. The electrolysis should take place at about 100°C and at a pH value 0 to 1.5. The current densities proposed would be 5 A/dm^2 (up to 73 A/dm^2).

M.B. Pell and R.W. Blossom [37] doubt the possibility of achieving according to the method indicated in [36] a uniform accumulation of nickel hydroxide inside the pores. They indicate as optimum current density for electrodes 0.75 mm thick at room temperature, the value of 1.55--2.33 A/dm^2. This should provide a maximum capacity of 0.27--0.31 Ah/cm^3 for a duration of the electrolysis of 6 to 7 hours. With the process they developed, they obtained capacities of 0.30--0.43 Ah/cm^3. They carry out a potentiostatic electrolysis using a silver/silver chloride reference electrode. According to the program the voltage is controlled in such a way that the initial current density is at 30 A/dm^2 with reference to the plate surface. The electrolyte contains 700--1150 g/ℓ nickel nitrate hexahydrate at pH values of 0--3 and temperatures of about 60°C. The filling process should last less than 10 minutes. The subsequent destruction of

nitrate in 25% KOH can also be carried out at increased temperature, specifically 90°C. Thus, this partial stage lasts about 20 minutes at 7 A/dm^2.

Apparently in the USA they are working on a large scale technical implementation of the modified Kandler process, since several members of the Bell Telephone Laboratories published recently a large number of articles in this area. Thus E.J. McHenry and R.L. Beauchamp [35] reported at the autumn conference of the Electrochemical Association of the USA on the "Process studies for the continuous electrochemical impregnation of nickel and cadmium electrodes at high temperatures." Their electrolytes received an addition of NaNO$_2$. The working temperature is near 80°C, the current density 7.75 A/dm^2. As was already indicated by D.M. MacArthur [32] and E.J. McHenry [34], the great importance of a highly wettable sintering structure is mentioned. Therefore the purification stage is included in the production cycle, which consists in boiling in 5% hydrogen peroxide or a cathodic electrolysis in a hot alkali solution. Table 1 gives a survey of the cathodic filling process.

F.P. Kober [28] was the first to use an anodic method. His electrolyte consists of nickel amino formate in alkaline solution. The pH value is maintained at 10 by adding 15% KOH. The current density is 10.05 A/dm^2 at 45°C. The mechanism proposed by Kober

$$Ni(NH_3)_x^{2+} + (3x - 2)OH^- \rightleftharpoons Ni(OH)_2 + x\,NO_3^- - 6x\,H^+ + 8x\,e^- \qquad (6)$$
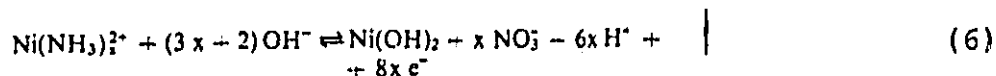
may rightly be called hypothetical.

2.3.3. Plating Bath

An interesting method not recommended by Kandler [25] was described by R.G. Black, J.L. Pentecost and H.S. Moore [4], which they used to produce the positive electrode thin film nickel-cadmium battery, a degenerated galvanic nickel bath (300 g/ℓ nickel sulfate,

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TABLE 1. SURVEY OF THE DIFFERENT CATHODIC FILLING PROCESSES FOR NICKEL HYDROXIDE ELECTRODES ABOUT 1 MM THICK

Literature	Electrolyte without $Co(NO_3)_2$	pH	Temperature °C	Current density A/dm^2	Electrolysis	Capacity obtained	Characteristics
[22,25]	100 g/ℓ $Ni(NO_3)_2 \cdot 6H_2O$	2-3	25	0.5	8 h	1.65 Ah/dm^2	Slow regression of the current density
[9]	2 parts 1 m $Ni(NO_3)_2 \cdot 6H_2O$ 1 part 25% NH_4OH	9-12	25	5	4-5 h	?	
[36]	$Ni(NO_3)_2 \cdot 6H_2O$ melted	0-1.5	100	5	2-3 h	?	
[37]	1100 g/ℓ $Ni(NO_3)_2 \cdot 6H_2O$ 1 g/ℓ increase of carbon U.C. 600	0-3	80	30	10 min	0.27-0.31 Ah/cm^3	Potentiostatic against Ag/AgCl
[34]	4 m $Ni(NO_3)_2 \cdot 6H_2O$	0	25	17	5-10 min	?	Purification of the sintered plates before impregnation.
[35]	2 m $Ni(NO_3)_2 \cdot 6H_2O$ 0.3 m $NaNO_2$	4	70-80	7.75	40 min	?	Purification of the sintered plates before impregnation.

20 g/ℓ nickel chloride, 20 g/ℓ nickel ammonium sulfate and 30 g/ℓ nickel formate). For a pH value of 1.5--3.5, a temperature of 18--21°C and a current density of 1--5.4 A/dm^2, a mixture of nickel hydroxide and nickel is obtained at the cathode.

3. Microscopic Investigations

Microscopic investigations of the positive electrode were carried out with different types of equipment, and specifically among others, by E. Häusler [22], N.E. Bagshaw, M.I. Gillibrand and K.P. Wilson [2], K.D. Beccu and H. Stöhr [3], S.U. Falk and A.J. Salkind [16], also E.J. McHenry [34]. The sintering structure without hydroxide accumulation was studied by S.M. Rachovskaya et al. [39], G. Halpert [20] and N. Svate [43]. Of all the methods used here, scanning electron microscopy (SEM) proved to be the most impressive because of the high depth sharpness. The SEM photographs allow, even with 10,000--30,000-fold enlargement, sufficient

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information to be obtained on the spatial arrangement in the porous plate.

Since electrochemically filled postive electrodes have not been studied hitherto by scanning electron microscopy, it seemed to us rewarding to carry out such investigations ourselves. For our photographs we used the SEM-Universal 3 instrument of the Jeo Company [41]. The production of the samples was very simple. From the sintered electrode plates to be studied, small pieces were broken off, mounted with the ruptured side in which we were interested on top on the sample holder, and in the case of hydroxide inclusions covered by means of evaporation with gold up to a layer of 500--1000 Å.

3.1. The Empty Sintering Frame

To have an impression of the basic material of our electrodes the sintering frame was first considered. Figure 4 shows a light microscopy cross section through the type of electrode used most frequently by us without hydroxide filling. We refer to a sintering frame of carbonyl nickel with a porosity of about 80% and a real area of about 1 m^2/cm^3. The pore diameter is 5--10 μm. The grains on the average are 3 μm, the perforated nickel plate 0.08 mm and the total plate 1.1 mm thick.
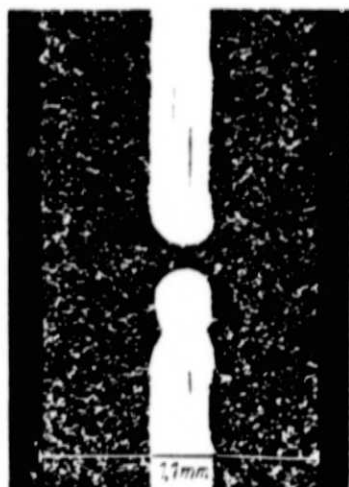

Figure 4. Cross section through a plate of sintered nickel. The nickel grains are white. In the middle the pierced nickel supports a plate. Light microscope enlargement about 50-fold.

In the SEM photograph (Figures 5 and 6) the sintering areas of the individual nickel grains can be recognized, which cause the mechanical adhesion of the electrode and the high electrical conductivity. The breaks on the edge of the picture come from grains which were damaged in preparation.

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Figure 5. Scanning electron
micrograph of a
rupture through a sintered
nickel plate: some nickel
grains are broken by the
preparation. Enlargement
5,000-fold.

Figure 6. Same as Figure 5.
Enlargement 10,000-fold.
Nickel grains are 1--3 μm.

3.2. The Nickel Hydroxide Electrodes

Here too a type of survey
picture was produced by the method
of conventional electron microscopy
with a slide through an electrode
filled with nickel hydroxide according
to the Kandler process
(Figure 7). The carbonyl nickel
grains appear to be white, likewise
the supporting plate on the right
hand side of the picture. The
accumulated nickel hydroxide has a
light to dark grey tone. The nickel
hydroxide plates used for the microscopic
investigations come from the
cells whose discharge characteristics
may be seen in Figure 3. The electrodes
were therefore exposed to
about 12 charging and discharging
cycles. Figures 7, 8, 9 and 12 show
the positive mass in the discharge
state, Figure 13 shows the oxidized
state.

In Figures 8 and 9 we are
struck primarily, as compared with
Figures 10 and 11, by the spherical
well-arranged structure imposed on
the basic frame. Figures 10 and 11
give an insight into pores of a
chemically filled electrode of the
storage battery of Figure 2. This
positive mass is also in the discharge
state. Obviously here the hydroxide crystals are entangled,
the material does not appear to be structurized. We have the

Figure 7. Cross-section of a nickel sintered plate filled with nickel hydroxide according to the Kandler method; nickel grains white, active mass grey, on the right hand side the pure nickel supporting plate. Electron microscopic enlargement about 800-fold.

Figure 8. SEM photograph of a break through a nickel sintered plate filled with Ni(II)hydroxide according to the Kandler process. Enlargement 5,000-fold.

impression that the nickel basic frame may be "smeared".

Both types of electrodes were studied over the entire width of the break. The piture practically did not change for the chemically activated electrode, which was filled relatively uniformly over the entire thickness. The electro-chemically activated electrode, on the other hand, was filled most densely in the vicinity of the nickel support coil, therefore in the center, and was clearly more open outwardly. A glance at one of the external sides of the electrode showed a relatively wide open pore. Only little hydroxide was found on the other side. Things were different for the chemically filled electrodes; here even the external pores, apart from a few exceptions, were almost closed.

It was a lucky coincidence that some of the hydroxide "sponges" of the electrochemically filled electrode broken off in the preparation came into the field of vision. Figure 12 shows such a broken sponge of the discharge electrode, Figure 13 one of the charged ones. It is clearly apparent that the hydroxide sponge is "grown on" the carbonyl nickel grain. The structure of
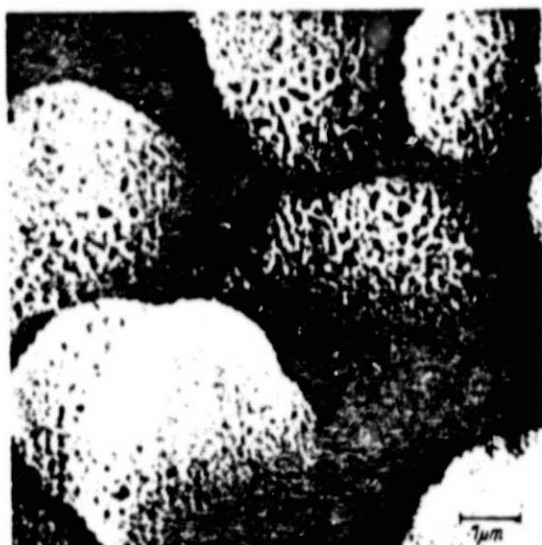
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Figure 9. Like Figure 8.
Enlargement 10,000-fold.

the surface of the hydroxide
layer continues with very fine
channels inwardly until the nickel
grain. The comparison with a
sponge seems to be justified in
this connection.

It is striking to note the ab-
sence of a difference in structure
of the oxidized and reduced forms
(Figures 12 and 13). Only the volume
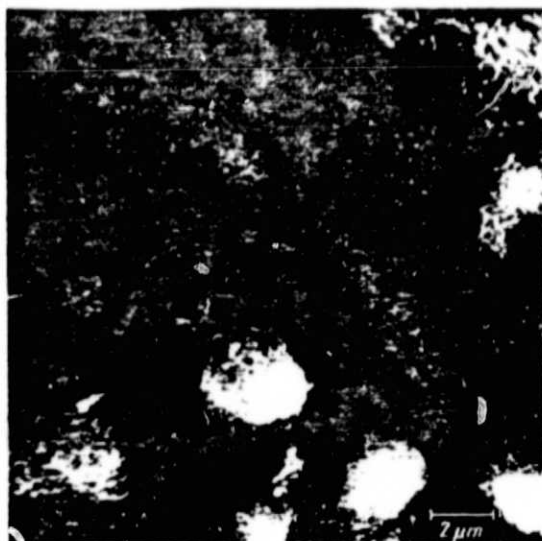of the sponge has increased in the
charging.

Figure 10. SEM photograph
of a break through a nickel
sintered plate filled with
Ni(II)hydroxide according to
the impregnation method.
Enlargement 5,000-fold.

Figure 11. Like Figure 10.
Enlargement 10,000-fold.

Figure 12. SEM photograph of a nickel(II)hydroxide sponge of Figures 8 and 9 produced according to the Kandler method, the sponge is broken off in the preparation and dissolved away by the carbonyl-nickel grain. Enlargement 10,000-fold.

Figure 13. SEM photograph of a nickel(II)hydroxide sponge produced by the Kandler method; the sponge was broken off in the preparation and partly detached from the nickel grain. Enlargement 10,000-fold.

4. Discussion

The technical importance of the nickel-cadmium storage battery has inspired a large number of publications on the structure and mechanism of the positive electrode [30, 21, 27, 40, 1 among others]. In particular H. Bode, U. Dehmelt and J. Witte [5, 6], D.J. Tuomi [45] and W. Dennstedt and W. Löser [10] recently studied the structure of the different nickel hydroxides and hydroxides. The fact that in the real case of charging and discharging of the positive plate, relatively few difference exist in the appearance of structure between the two charging states, has been shown by N.B. Bagshaw, M.J. Gillibrand and K.P. Wilson [2], G.W. Briggs, G.W. Stott and W.F.K. Wynne-Jones [7, 8], also F.P. Kober [27] microscopically, by X-rays and thermogravimetrically. Even with a 30,000-fold SEM enlargement we were unable to establish a different structure. Figures 12 and 13 give an impression of this. In the charging process we only observed a swelling of sponge, an increase in volume. Even

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the color remains the same.

According to [5, 6] in the chemical precipitation, β-hydroxide containing water is chiefly separated. D.M. MacArthur [31, 33] finds predominantly α-nickel hydroxide in the electrochemical precipitation (more exactly nickel(II)hydroxide hydrate). The theoretical water content of the α-hydroxide is 28.6%, that of β-hydroxide 19.4%. The mechanism of transition from the discharged to the charged state proposed by Bode [5, 6] was confirmed by W. Dennstedt and W. Löser [1]. Water molecules are taken up into the lattice and the latter is thus extended (also [27, 45]). In a simplified form we can write the discharge-charge mechanism in the following form:

$$2\,NiOOH + 2\,H_2O + 2\,e^- \underset{charge}{\overset{discharge}{\rightleftharpoons}} 2\,Ni(OH)_2 + 2\,OH^- \tag{7}$$
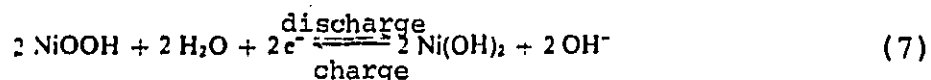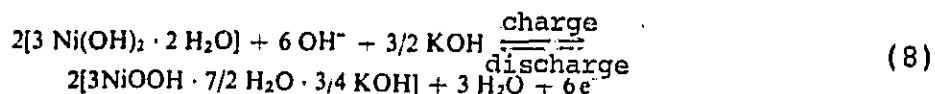
The consumption of water in the electrolyte, which was determined by G. Krämer [29] in the loaded sintered foil electrodes, is 0.47 mols per Faraday in the discharge. To reduce the concentration polarization, therefore, care must be taken for the fastest possible removal from the electrolyte. From Figures 8 and 9, as well as 10 and 11 we can recognize for this case the great superiority of the electrochemically filled positive plates as compared with the chemically filled ones. The diffusion is favored to the maximum extent in the electrochemically filled plates. The pores are very wide outwardly, and even the hydroxide layers show fine pore structures until the nickel core (Figures 12 and 13). Through the uniformly small distance from the nickel structure the charge transport of the hydroxide to the lattice is faciliated to a great extent.

Here according to K.J. Euler [14] a very favorable current distirbution should take place inside the electrode. Euler indicated that in the discharge of a compressed electrode, the electrode layer near the electrolyte appears very nonuniform. On the

other hand, for a chemically filled sintered electrode, a more
uniform current distribution was obtained right from the beginning.
Euler also indicates in this connection the decisive role of
diffusion.

In conclusion it may further be mentioned that according to the
latest investigation on the charging-discharging mechanism
indicated in a simplified form in equation (7), a controlled pro-
ton diffusion takes place in the lattice. H. Ewe and R. Kalberlah
[15] determine the diffusion coefficient of the proton $D=3 \cdot 10^{-5}$ cm^2/
sec. D.M. MacArthur [31, 32, 33] indicates the proton diffusion
coefficient as $3.1 \cdot 10^{-10}$ cm^2/sec during the charging process and
as $4.6 \cdot 10^{-11}$ cm^2/sec during the discharge. The protons move
through thermal diffusion in the lattice. Z. Takehara, M. Kato
and S. Yashizawa [44] confirm the findings of MacArthur and Ewe,
but consider a diffusion of defective protons. They measure with
i_o=232--322 mA/cm^2 a relatively high exchange current density in
the charging and discharging processes.

For the α-nickel hydroxide precipitated according to the
Kandler process, MacArthur, [51] indicates the following overall
reaction:

$$2[3 Ni(OH)_2 \cdot 2 H_2O] + 6 OH^- + 3/2 KOH \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} 2[3NiOOH \cdot 7/2 H_2O \cdot 3/4 KOH] + 3 H_2O + 6e^- \qquad (8)$$

5. Summary

In an analysis of the literature and by means of scanning
electron micrographs, the superiority of an electro-
chemically filled nickel hydroxide sintered electrode as compared
with chemically treated ones was shown. The chemically separated
nickel hydroxide is filled in a relatively uncontrolled manner in
the pores of the electrode. The hydroxide produced according to
the Kandler process is, on the other hand, grown mainly on the nickel
grains and has a well defined pore structure. Diffusion and
conduction mechanisms are thus favored. The photographs

were taken with the duration which has become known since
then regarding the structure and mechanism of the positive electrode
and contribute further to a more detailed knowledge of the latter.

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